

# Processes in spark electric discharge in air, nitrogen and oxygen

I M Piskarev<sup>1,3</sup> and N A Aristova<sup>2</sup>

<sup>1</sup> Skobeltsyn Institute of Nuclear Physics, Leninskie Gory, MSU, 1 (2), Moscow, 119234, Russia

<sup>2</sup> Ural Federal University named after the First President of Russia B N Yeltsin, Nizhniy Tagil Technological Institute, 59, Krasnogvardeyskaya str., Nizhniy Tagil, 622000, Russia

E-mail: <sup>3</sup> i.m.piskarev@gmail.com

**Abstract.** The yield of redox reactions in aqueous solutions under the action of a remote spark discharge in the air, nitrogen and oxygen was studied. Mohr's salt and potassium permanganate were used as test substances. The direct and indirect effects of a source of active particles were compared. On direct exposure active species can immediately interact with the substance. By indirect action the source of active species directly affects only water. Immediately after treatment water was mixed with a solution of the test substance and the reactions of accumulated active species with the test substance began. When discharged in air medium, the oxidation and reduction reaction yields are approximately the same  $5 - 6 \cdot 10^{-1} (100 \text{ nB})^{-1} \text{ eV}$ . Equal yields means that active species are firstly produced in water. When discharged in the nitrogen and oxygen medium, the oxidation yield is  $\sim 15\%$  lower, and the recovery yield is much lower. In this case, there is oxygen or nitrogen in the aqueous solution, so nitrogen oxides cannot be formed in water. So the contribution of products, produced in the discharge region is not more than  $15\%$  and that radiation plays a major role in initiating of chemical processes in liquid.

## 1. Introduction

Cold plasma and plasma activated water (PAW) have great prospects for their wide application and therefore are intensively researched [1, 2]. When producing PAW, the plasma is in direct contact with water [3]. The plasma used for this treatment (gliding arc plasma in particular) has dim light, so the role of radiation in the formation of PAW is considered to be insignificant. The oxidation of methyl orange with gliding arc plasma was studied in this paper [4]. After treatment there is a strong post-effect, which lasts up to 1 hour. It is noted that this effect is due to nitrogen oxides, but the mechanism of their formation and the role of the gas medium were not considered. The influence of nanosecond discharge plasma treatment of seeds in the air was studied in work [5]. A significant improvement in seed germinating ability was obtained. The discharge has not been optimized in terms of the choice of the gas medium. In work [6] Advanced Oxidation Technology variant of purification of waste water with the aid of a discharge inside the liquid is considered. It can be assumed that the efficiency of the process will depend on the degree of saturation of water with the gas mixture and the composition of this mixture.

The most potent oxidative agent formed in electric discharge plasma is peroxynitrite and peroxynitrous acid. These reagents can be formed if there is nitrogen and oxygen in the gas phase. The



properties of peroxinitrite and peroxinitrous acid are analysed in the overview [7]. In the case when there is no oxygen or nitrogen in the gas phase where the electric discharge occurs, only hydroxyl radicals can be formed. The formation of hydrogen peroxide under the action of light radiation in water containing dissolved nitrogen and oxygen was experimentally found in work [9]. A mechanism for forming hydrogen peroxide in water is proposed in [10]. It has been shown that hydrogen peroxide can be formed by radiation with wavelengths of 200 to 1260 nm, provided that there is dissolved oxygen in the water.

Studies [11, 12] established a strong chemical effect created in water and aqueous solutions by a spark electric discharge generator in air. The effect can be due both to the radiation of the plasma in liquid itself and to the nitrogen oxides diffusing from the discharge area. Nitrogen oxides are formed due to the Zeldovich mechanism in the discharge area containing nitrogen and oxygen in the air [13]. They can diffuse from the discharge area and give a direct contribution to the chemical action of electric discharge plasma.

Thus, studies have shown that the gas medium in which the electric discharge occurs has a significant influence on the properties of the processes under this discharge. Therefore, it is of interest to obtain additional information about the role of processes under the action of radiation only and the combined action of radiation and nitrogen oxides diffusing from the discharge area. For this purpose we have performed experiments with spark electric discharge in the air and in the medium of gases: separately in the medium of nitrogen and oxygen. When discharged only in nitrogen or only in oxygen, the Zeldovich mechanism of nitrogen oxide formation does not work, and the whole effect in the treated liquid will be determined only by the radiation of the plasma.

## 2. Materials and methods

The block-scheme of the experimental setup is shown in figure 1. A source of pulsed radiation was the generator of spark discharge SD50 [11, 12]. The spark discharge occurred between solid electrodes connected with the discharge capacitor  $C = 680$  pF. A high voltage power of 11 kV was supplied to the capacitor via a ballast resistor  $R = 8$  M  $\Omega$ . When the high voltage was turned on, a self-supporting spark discharge began. Full duration of current pulse was 5  $\mu$ s, leading edge was about 50 ns, energy of pulse  $8.1 \times 10^{-3}$  J, pulse repetition frequency was 50 Hz, discharge power was 0.4 J/s. The duration of the current pulse was determined by the time of charge dissipation. The current consumed from a high voltage power supply was  $0.7 \pm 0.02$  mA.

When discharged in a gas medium (nitrogen or oxygen), the reaction cavity and the cavity with the solution to be treated were purged with these gases. The liquid sample was saturated with dissolved gas, which was used for purging (only with nitrogen, or only with oxygen). Technical nitrogen (purity 99.6%) and technical oxygen (purity 99.7%) from the cylinder were used for purging. The time spent on gas purging before turning on the discharge was 16 minutes.

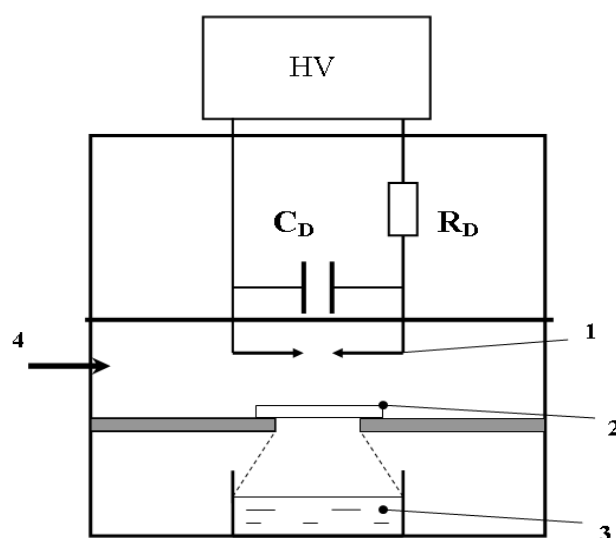
Direct and indirect effects of the source of active species were compared in this work. The direct effect means that the source affects directly the sample with the dissolved sample substance, the active species can interact with the substance at once. The indirect effect means that the source of active particles has a direct effect only on water. In indirect effect, active particles form and accumulate in water. Immediately after treatment, the water was mixed with the solution of the sample substance, where the reactions of the accumulated active species with the sample substance began.

To determine the chemical effect, oxidation-reduction reactions with sample substances were used. As sample substances, aqueous solutions of Mohr's salt and potassium permanganate were used. The yield of oxidative equivalents, formed during treating, was determined in the sample by the oxidation of ferrous iron in Mohr's salt  $\text{Fe}^{+2} \rightarrow \text{Fe}^{+3}$ . The yield of recovery equivalents was determined by the reduction of manganese  $\text{Mn}^{+7} \rightarrow \text{Mn}^{+2}$  in solution of potassium permanganate.

The concentration of Mohr's salt was 20 g / l,  $[\text{Fe}^{+2}] = 5.1 \cdot 10^{-2}$  mol / l. The concentration of potassium permanganate used in the treatment was 1.58 g / l (0.05N). 21 ml / l of concentrated sulfuric acid (0.4 M) was added to the solutions. The concentration of oxidized  $\text{Fe}^{+3}$  was determined by the

optical density of the band 304 nm,  $\varepsilon = 2100 \pm 50 \text{ L (mol cm)}^{-1}$ . The concentration of potassium permanganate was determined by the optical density of the band 527 nm,  $\varepsilon = 2160 \pm 50 \text{ L (mol cm)}^{-1}$ .

Absorption spectra of the samples were measured with a SF-102 spectrophotometer manufactured by AKVILON, Russia. The thickness of the cuvette was 10 mm. The optical density  $A = \lg(I_0/I)$  (Bel) was measured relative to distilled water. The pH value was measured by an Expert-001 device manufactured by EKONIKS, Moscow, Russia. Chemically pure reagents were used with twice distilled water at pH = 6.5. For each mode, 10 samples were generated; the results were averaged.

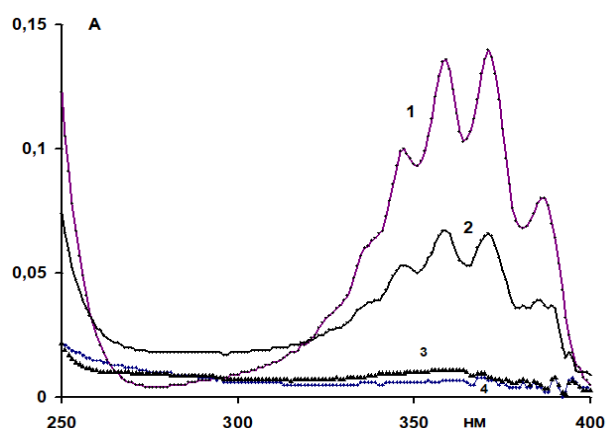


**Figure 1.** Block-scheme of the experimental setup. HV – high-voltage source 11 kV;  $C_D$ ,  $R_D$  – discharge capacity and ballast resistor; 1 – discharge electrodes; 2 – location of silica glass; 3 – Petri dish with processed liquid; 4 – gas purging (nitrogen or oxygen), except discharge in air medium.

### 3. Results and discussion

The mechanisms of the interaction of active species formed in water under the action of the SD 50 generator with sample substances are analyzed. It was shown that chain reactions of oxidation of sample substances do not take place. All reactions are slow; the total reaction yield was determined 3 days after treatment.

The absorption spectra of water samples with a volume of 5 ml after treating with a remote plasma discharge of the SD 50 generator for 3 minutes are presented in Fig. 2. It is seen that during the discharge in the air medium, nitrous acid is forming (Curve 1), the acidity of the sample is pH = 2.47. When discharged in a nitrogen and oxygen medium, traces of nitrous acid are not visible (Curves 3 and 4), the acidity of the samples remains at the initial level, pH = 6.5. The absence of nitrous acid under these conditions is due to two circumstances. Firstly, nitrogen oxides do not form in the discharge region, since in pure nitrogen or pure oxygen the Zeldovich mechanism of the formation of  $\text{NO} \cdot$  and  $\text{NO}_2 \cdot$  does not work. And secondly, since the sample contains only dissolved nitrogen or only dissolved oxygen, the mechanism of formation of nitrogen-containing compounds under the action of radiation in the liquid which contains dissolved nitrogen and oxygen also does not work.



**Figure 2.** Water absorption spectra

1 - discharge in the air medium; 2 - discharge in the air medium, yield of radiation through quartz glass; 3 - discharge in nitrogen; 4 - discharge in oxygen.

Separately, a water sample was processed through quartz glass. In this case, the products formed in the discharge region could not get to the surface of the sample. The sample was in the air, so dissolved oxygen and nitrogen were contained in the water itself. The absorption spectrum of the sample after 3 minutes of processing is shown in Fig. 1, Curve 2. It is seen that in this case nitrous acid is formed, but its optical density is approximately two times lower. This may be due to the fact that quartz glass absorbs radiation, the optical density of the glass at wavelength of 200 nm is  $A \sim 0.19$ . It may also be because nitrogen oxides formed in the discharge region cannot contribute to the formation of nitrous acid.

Taking into account the stoichiometry of the reactions, the oxidation and reduction yields were calculated in Table 1. The table shows that in the case of discharge in air, the oxidation and reduction yields are the same for direct and indirect action. Equality of yields means that active species are first produced in water, and then interact with a sample substance that is directly contained in the solution, or added after treatment.

**Table 1.** Oxidation and reduction yields in the solutions of sample substances under the action of the SD 50 generator, 1 / (100 eV)

Discharge conditions	Direct effect		Inirect effect	
	Oxidation	Reduction	Oxidation	Reduction
In air	$5.7 \pm 0.9$	$6.2 \pm 1$	$6.1 \pm 0.9$	$5.6 \pm 0.9$
In nitrogen	$3.7 \pm 0.7$	$0.47 \pm 0.05$	$5.7 \pm 0.9$	$0.27 \pm 0.03$
In oxygen	$1.35 \pm 0.3$	$0.5 \pm 0.1$	$4.53 \pm 0.8$	$0.1 \pm 0.015$

The oxidation yields of the discharge in nitrogen medium for direct and indirect effect are less than  $\sim 15\%$  of the discharge in air medium. This means that the role of nitrogen-containing compounds formed in the discharge region in the air medium and diffusing to the sample surface is small and does not exceed  $\sim 15\%$ .

The recovery yield for the discharge in nitrogen or oxygen medium in all treatment modes is almost an order less than the oxidation yield. The features of the reactions in these cases may be due to the fact that there is only oxygen or only nitrogen in the aqueous solution, and nitrogen oxides cannot form in water. It follows that the nitrogen-containing compounds formed from them under the action of radiation in the case of discharge in air play an important role in oxidation-reduction processes.

Radiation plays the major role in the oxidation-reduction processes under the influence of the spark discharge generator SD 50.

The main reaction mechanism under the action of radiation is indirect, when active species are first formed in liquid, and then enter into reactions.

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